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[54] 发明名称 用于锂离子电池的正极的改性锂钴氧化物及其制备方法和锂离子电池

[57] 摘要

本发明是关于一种具有层状岩盐型 (α - NaFeO_2 型) 结构的锂钴氧化物 (LiCoO_2)；尤其有关一种改性锂钴氧化物。一种改性锂钴氧化物，当其被用作为锂离子电池的正极时，可提高锂离子电池的充电电位至 4.4V。该改性锂钴氧化物包括锂钴氧化物颗粒及附着于该颗粒的表面上的 ZrO_2 、 TiO_2 、 B_2O_3 、 Al_2O_3 或 Ga_2O_3 。该改性锂钴氧化物是通过将锂钴氧化物颗粒浸渍于一含有 Zr、Ti、B、Al 或 Ga 的离子的水溶液，及煅烧该被浸渍的锂钴氧化物颗粒而制备。

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1. 一种改性锂钴氧化物，包含：锂钴氧化物颗粒及附着于该颗粒的表面的 MO_x ，其中 M 为 Zr, Ti, B, Al 或 Ga；及当 M 为 Zr 或 Ti 时， $x=2$ ，而当 M 为 B, Al 或 Ga 时， $x=3/2$ 。

2. 如权利要求 1 所述的改性锂钴氧化物，其中包含 0.5~15 重量% 的 MO_x 。

3. 如权利要求 2 所述的改性锂钴氧化物，其中该 MO_x 为 ZrO_2 或 B_2O_3 。

4. 一种锂离子电池，包含一正极，该正极包含改性锂钴氧化物，该改性锂钴氧化物包含：锂钴氧化物颗粒及附着于该颗粒的表面的 MO_x ，其中 M 为 Zr, Ti, B, Al 或 Ga；及当 M 为 Zr 或 Ti 时， $x=2$ ，而当 M 为 B, Al 或 Ga 时， $x=3/2$ 。

5. 如权利要求 4 所述的锂离子电池，其中该改性锂钴氧化物包含 0.5~15 重量% 的 MO_x 。

6. 如权利要求 5 所述的锂离子电池，其中该 MO_x 为 ZrO_2 或 B_2O_3 。

7. 一种改性锂钴氧化物的制备方法，该改性锂钴氧化物包含锂钴氧化物颗粒及附着于该颗粒的表面的 MO_x ，其中 M 为 Zr, Ti, B, Al 或 Ga；及当 M 为 Zr 或 Ti 时， $x=2$ ，而当 M 为 B, Al 或 Ga 时， $x=3/2$ ，该方法包含将锂钴氧化物颗粒浸渍于一含有 Zr, Ti, B, Al 或 Ga 离子的水溶液中；及煅烧所获得的被浸渍过的锂钴氧化物颗粒，于是形成该改性锂钴氧化物。

8. 如权利要求 7 所述的制备方法，其中该锂钴氧化物颗粒被浸渍在 $\text{ZrO}(\text{NO}_3)_2$ 水溶液或硼酸水溶液。

9. 如权利要求 7 所述的制备方法，其中该被浸渍过的锂钴氧化物颗粒在该煅烧之前先在一升高温度下被干燥，及该煅烧是在 $400\sim 800^\circ\text{C}$ 进行 1~5 小时。

10. 如权利要求 9 所述的制备方法，其中该煅烧是在 600°C 进行 3

小时。

11. 如权利要求 7 所述的制备方法, 其中该改性锂钴氧化物包含 0.5~15 重量%的 MO_x 。
12. 如权利要求 11 所述的制备方法, 其中该 MO_x 为 ZrO_2 或 B_2O_3 。

用于锂离子电池的正极的改性锂钴氧化物及其制备方法和锂离子电池

技术领域

本发明是关于一种具有层状岩盐型(α - NaFeO_2 型)结构的锂钴氧化物(LiCoO_2)；尤其有关一种改性锂钴氧化物，当其被用作为锂离子电池的正极时，该锂离子电池具有约 4.4V 的充电电位。

背景技术

由于可充电锂离子电池的优异能量密度，它们目前已经广泛用于便携式电子设备例如移动式电话及笔记本型计算机的可充电能源。

目前的锂离子电池大都使用具有层状岩盐型(α - NaFeO_2 型)结构的 LiCoO_2 作为正极，一碳材料例如石墨作为负极，及含有 Li 盐的一有机物溶液作为电解质。该 LiCoO_2 一般是通过在 700~900℃ 煅烧一含有钴氧化物及碳酸锂的混合物而制备。使用此 α - NaFeO_2 型结构的 LiCoO_2 作为正极的锂离子电池其充电电位约 3.8 至 4V。如果该煅烧温度是在约 400℃ 左右，则所制得的锂离子电池的充电电位会降至约 3.5V。由于高的煅烧温度会导致 LiCoO_2 产率下降，而低的煅烧温度又不利于所制得的锂离子电池的充电电位，因此遂有研究者提出一种水热氧化法(hydrothermal oxidation)在较低的温度下约 160~300℃ 来制备层状岩盐型 LiCoO_2 ，例如美国专利第 6,399,041 B1 号。然而，此水热氧化法的制备较为复杂。所以，在业界中存在着一种需要即是一种可提高以层状岩盐型 LiCoO_2 作为正极的锂离子电池的充电电位的技术。该技术不仅可以使制备 LiCoO_2 的煅烧的温度降低；也可使目前使用 LiCoO_2 作为正极的锂离子电池具有更高的充电电位，于是延长电池的使用时间。

发明内容

本发明的一主要目的在于提出一种改性锂钴氧化物,当其被用作为锂离子电池的正极时,可提高锂离子电池的充电电位,例如 4.4V。

本发明的另一目的在于提出一种改性 LiCoO_2 的制备方法。

本发明的又一目的在于提出一种锂离子电池其具有改善的充电电位,例如 4.4V。

为了实现上述发明目的,依照本发明所完成的改性锂钴氧化物包含:锂钴氧化物颗粒及附着于该颗粒的表面上的 MO_x ,其中 M 为 Zr, Ti, B, Al 或 Ga; 及当 M 为 Zr 或 Ti 时, $x=2$, 而当 M 为 B, Al 或 Ga 时, $x=3/2$ 。

本发明提出一种锂离子电池,包含一正极,该正极包含本发明的改性锂钴氧化物。

本发明亦提出一种改性锂钴氧化物的制备方法,包含将锂钴氧化物颗粒浸渍于一含有 Zr, Ti, B, Al 或 Ga 离子的水溶液中; 及煅烧所获得的被浸渍过的锂钴氧化物颗粒。

较佳的,该改性锂钴氧化物包含 0.5~15 重量%的 MO_x 。若 MO_x 的含量小于 0.5 重量%,该改性锂钴氧化物相较于锂钴氧化物没有产生实质上的改性效果。若 MO_x 的含量大于 15 重量%则可能不利于改性锂钴氧化物作为锂离子电池的正极的表现。

较佳的,该 MO_x 为 ZrO_2 或 B_2O_3 。

在本发明的制备方法中,较佳的,该锂钴氧化物颗粒被浸渍于 $\text{ZrO}(\text{NO}_3)_2$ 水溶液或硼酸水溶液。

较佳的,在本发明的制备方法中该被浸渍过的锂钴氧化物颗粒,先在一升高温度下被干燥,再在 400~800℃煅烧 1~5 小时,更佳的在约 600℃煅烧 3 小时。

附图说明

图 1 为锂钴氧化物颗粒的扫描电子显微镜(SEM)的照片。

图 2 为锂钴氧化物的能量散布光谱(EDS)。

图 3 为本发明的改性锂钴氧化物颗粒的扫描电子显微镜(SEM)的照

片。

图 4 为本发明的改性锂钴氧化物的能量散布光谱(EDS)。

图 5 为电池放电比电容量(discharge specific capacity)对充放电循环次数的作图, 其中 a)使用附着有 B_2O_3 的 $LiCoO_2$ 作为锂离子电池的正极; b)使用附着有 ZrO_2 的 $LiCoO_2$ 作为锂离子电池的正极; c)使用一 $LiCoO_2$ 商品作为锂离子电池的正极。

具体实施方案

较佳具体实施例的详细说明

本发明以化学改性技术合成 $LiCoO_2-MO_x$, 其中 M 及 X 的定义同上。 $LiCoO_2$ 的制备方法已为业界所已知, 一典型的制备方法包括混合固态的工业级碳酸锂(Li_2CO_3)及四氧化三钴(Co_3O_4)颗粒, 及在 $600\sim 900^\circ C$ 煅烧该混合物 5~25 小时, 较佳的在 $800^\circ C$ 煅烧 10 小时, 形成纯相 $LiCoO_2$ 主体化合物。本发明进一步以水溶性先驱物(例如硝酸锆或硼酸)的水溶液浸渍 $LiCoO_2$, 再在 $400\sim 800^\circ C$ 煅烧 1~5 小时, 使水溶性先驱物中的 M 金属离子经高温氧化后, 形成附着在 $LiCoO_2$ 表面的 MO_x 氧化物, 亦即形成 $LiCoO_2-MO_x$ 。水溶性先驱物的一合适用量为使 $LiCoO_2-MO_x$ 含有 0.5~15 重量%的 MO_x 。

实施例 1: $LiCoO_2-ZrO_2$

将具有 90%粒径小于 17 微米的粒径分布的 $LiCoO_2$ 颗粒 1.9 克浸渍于含有 0.1 克 $ZrO(NO_3)_2 \cdot xH_2O$ (分子量 231.23, ALDRICH, 美国, 代号 34646-2)的水溶液 20 毫升中, 在 $110^\circ C$ 干燥所形成的混合物, 再将所获得的干燥混合物于 $600^\circ C$ 煅烧 3 小时。煅烧后的产物于研磨后即可作为锂离子电池的正极材料。

图 1 所示为未经修饰前的 $LiCoO_2$ 颗粒的 SEM 照片, 而图 2 则为其 EDS 光谱。从图 1 可看出 $LiCoO_2$ 颗粒的表面相当平滑, 而图 2 则显示氧及 Co 的峰。

修饰过的 $LiCoO_2$ 的 SEM 照片被示于图 3, 从其中可以看出 $LiCoO_2$ 颗粒的表面附着有物质。图 4 为该修饰过的 $LiCoO_2$ 的 EDS 光谱, 其中

除了氧及 Co 的峰外，亦显示出 Zr 的峰。

实施例 2: $\text{LiCoO}_2\text{-B}_2\text{O}_3$

除了以 0.1 克的硼酸(H_3BO_3 , 分子量 61.83)粉末(ALDRICH, 美国, 代号 23646-2)取代 0.1 克的 $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ 外, 重复实施例 1 的步骤。

使用实施例 1~2 及商品 LiCoO_2 (Nippon chemical Industrial Co., 日本, 代号 CELLSEED C), 制作正极, 以锂金属作为负极, 及以 EC (碳酸亚乙酯)及 DEC (碳酸二乙酯)混合溶剂的 1 M LiPF_6 溶液作为电解质, 组装 2030-Type 钮扣半电池。在 0.2C 的充放电速率(电流密度 28 mA/g)条件下测试。当以商品 LiCoO_2 材料作为正极的电池以高电位充放电时(3~4.4V), 虽然较低电位充放电(3~4.2V)可增加电池使用时间约 20%, 但经长循环测试时却发现如图 5(c)的现象, 亦即至约 70 次循环时, 放电比电容量大幅衰退。以本发明的改性 $\text{LiCoO}_2\text{-MO}_x$ 作为正极的电池, 在相同测试条件时, 结果如图 5 的(a)及(b)所示, 在 100 次循环测试后, M 为 B 时, 可保持 90%以上的初始放电比电容量, M 为 Zr 时则维持 81%的初始放电比电容量。

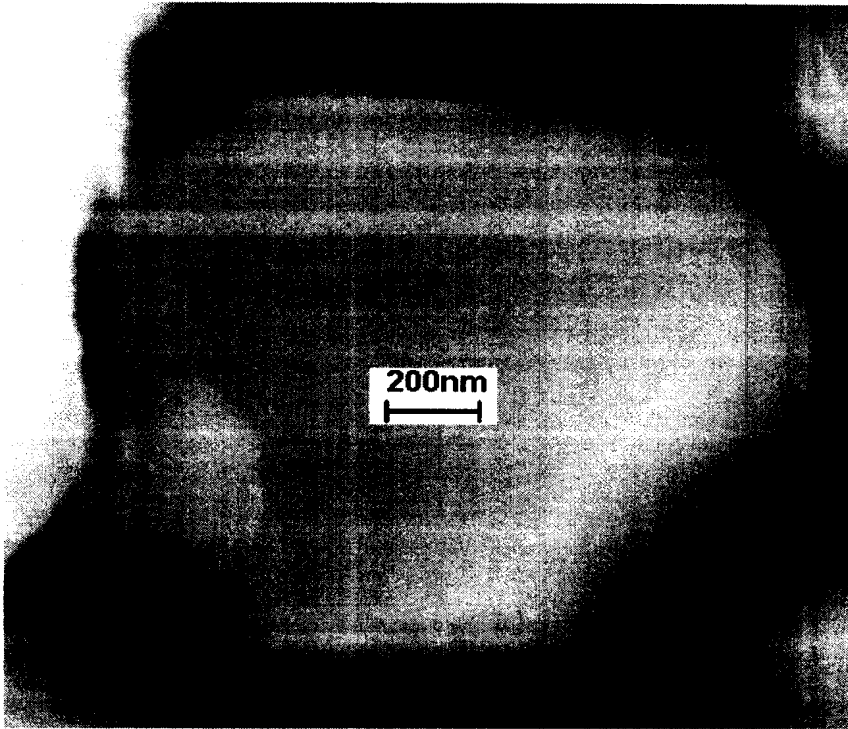


图 1

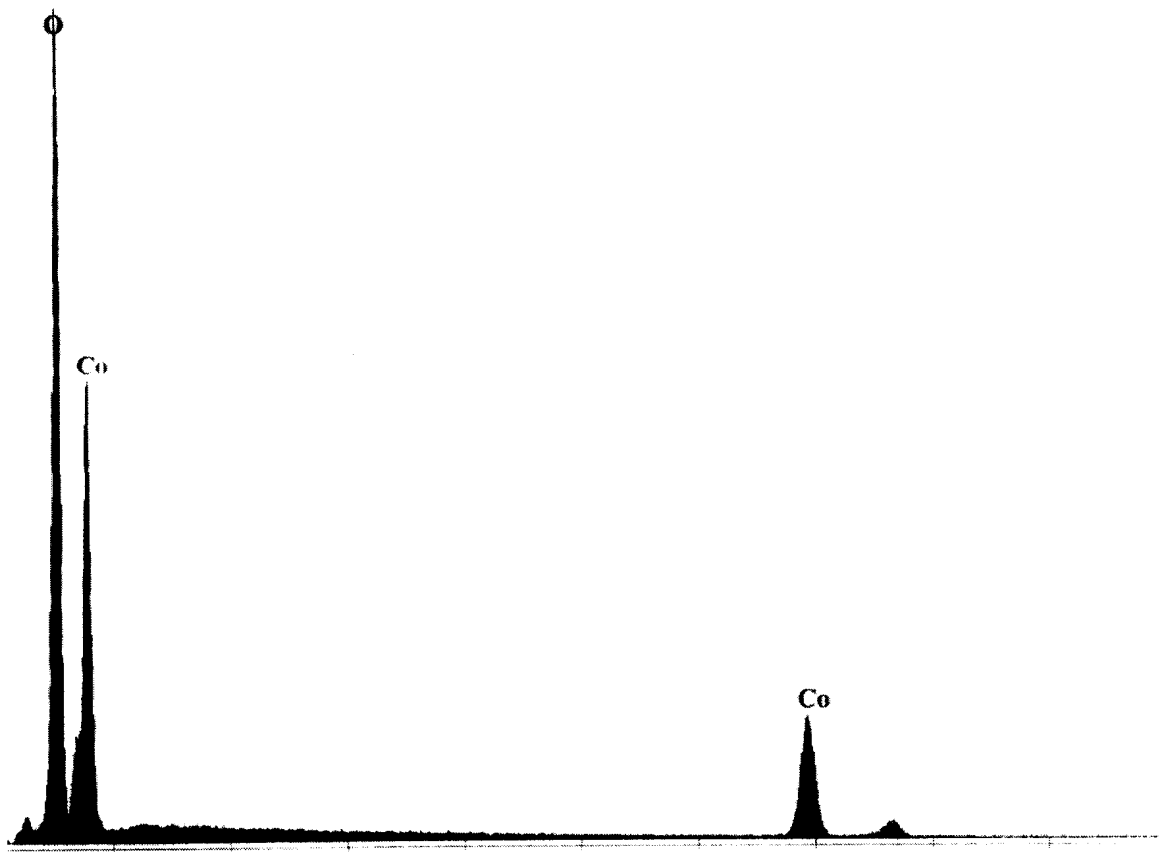


图 2

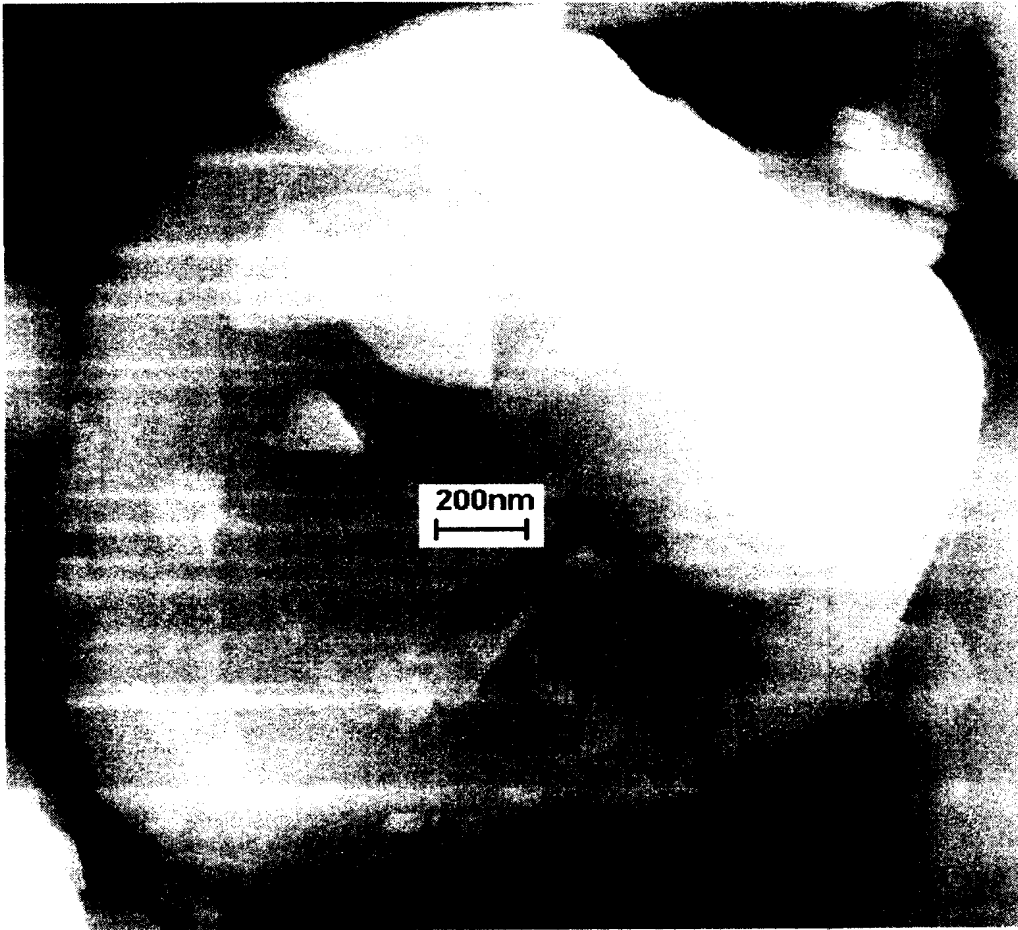


图 3

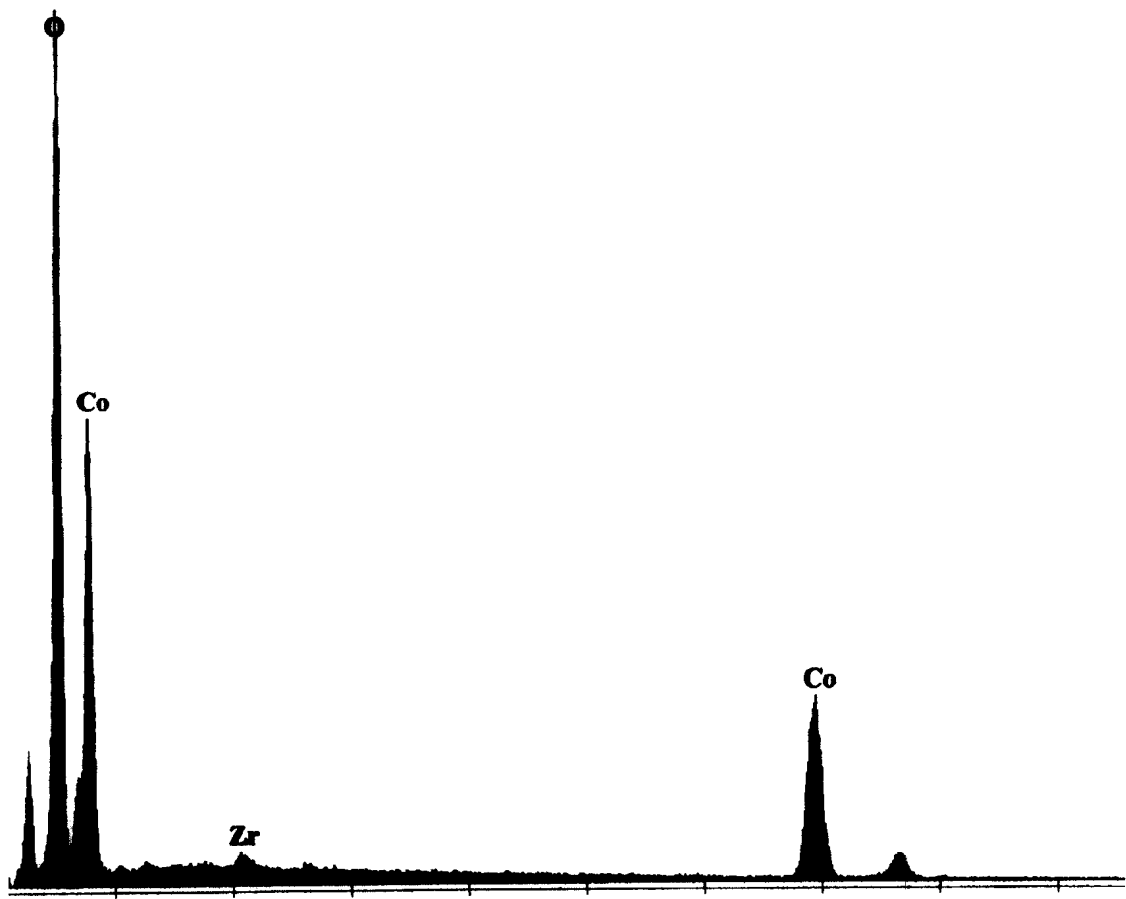


图 4

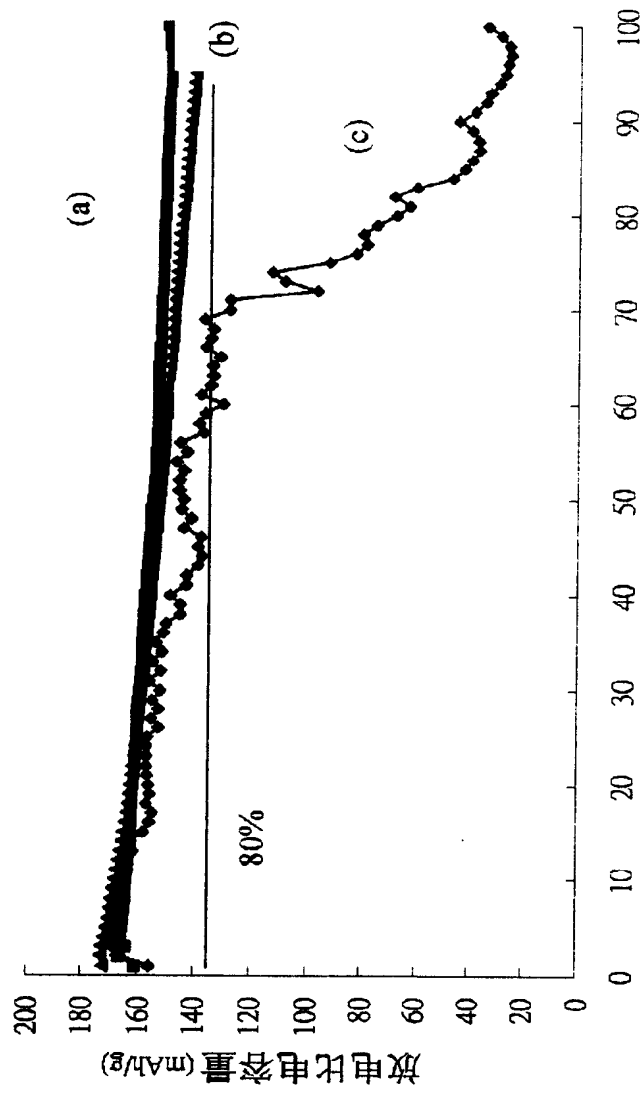


图 5

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TITLE: Modified lithium-cobalt oxide used for positive
pole of
lithium ion cell

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PATENT-ASSIGNEE: IND TECHNOLOGY INST[INTEN]

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BASIC-ABSTRACT:

NOVELTY - When lithium cobalt oxide (LiCoO₂) is used as the positive pole of a Li ionic battery, its charging potential can be increased to 4.4 V. The modified oxide includes LiCoO₂ particles and zirconia (ZrO₂), titania (TiO₂), boron oxide (B₂O₃), alumina (Al₂O₃) or gallium oxide (Ga₂O₃) adhered on the surface of the particles and is prepared by dipping the particles in a solution containing Zr, Ti, B, Al or Ga ions and burring the dipped particles.

TITLE-TERMS: MODIFIED LITHIUM COBALT OXIDE POSITIVE POLE ION CELL

DERWENT-CLASS: L03 X16

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EPI-CODES: X16-B01F1; X16-E01C1;

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SITE SEARCH



Modified lithium-cobalt oxide used for positive pole of lithium ion cell, its prepn and lithium ion cell

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Inventor(s) Name	Li Riqi,Lin Junren,Xu Zheyuan		
Patent Agency Code	31002	Patent Agent	li bai

Abstract

This invention relates to LiCoO₂ of laminated helite alpha-NaFeO₂ structure, especially to a modified LiCoO₂. When it is used as the positive of a Li ionic battery, its charging potential can be increased to 4.4v. The said modified oxide includes LiCoO₂ particles and ZrO₂, TiO₂, SnO₂, Al₂O₃ or Ga₂O₃ adhered on the surfaces of the particles and is prepared by dipping the particles in a solution containing Zr, Ti, B, Al or Ga ions and burning the dipped particles.

[Machine Translation](#) [Close](#)

Claim

1. modified lithium cobalt oxide contains: lithium cobalt oxide particle and attach to the MO on the surface of this granule_x, wherein M is Zr, Ti, B, Al or Ga; And when M is Zr or Ti, x=2, and work as M and be B, when Al or Ga, x=3/2.
2. modified lithium cobalt oxide according to claim 1 wherein contains 0.5 to 15 weight %'s MO_x.
3. modified lithium cobalt oxide according to claim 2, wherein this MO_x For ZrO₂ Or B₂O₃.
4. a lithium ion battery contains a positive pole, and this positive pole contains modified lithium cobalt oxide, should contain by modified lithium cobalt oxide: lithium cobalt oxide particle and attach to the MO on the surface of this granule_x, wherein M is Zr, Ti, B, Al or Ga; And when M is Zr or Ti, x=2, and work as M and be B, when Al or Ga, x=3/2.
5. lithium ion battery according to claim 4 wherein is somebody's turn to do the MO that modified lithium cobalt oxide contains 0.5 to 15 weight %_x.
6. lithium ion battery according to claim 5, wherein this MO_x For ZrO₂ Or B₂O₃.
7. the method of preparation of a modified lithium cobalt oxide is somebody's turn to do the MO on the surface that modified lithium cobalt oxide contains lithium cobalt oxide particle and attaches to this granule_x, wherein M is Zr, Ti, B, Al or Ga; And when M is Zr or Ti, x=2, and work as M and be B, when Al or Ga, x=3/2, this method contains to flood lithium cobalt oxide particle in one and contains Zr, Ti, B is in the Al or the Ga ionic aqueous solution; And calcine gained by impregnated lithium cobalt oxide particle, so form should modified lithium cobalt oxide.
8. the method of preparation of claim 7, wherein this lithium cobalt oxide particle is flooded (the NO at ZrO₃)₂ The aqueous solution or the boric acid aqueous solution.
9. the method of preparation of claim 7, wherein should by impregnated lithium cobalt oxide particle earlier by dry under the rising temperature before this is calcined, and should calcine and carry on 1 to 5 hour 400 to 800 DEG Cs.
10. the method of preparation of claim 9 wherein should be calcined and carry on 3 600 DEG Cs

Claim

Hour.

11. the method of preparation of claim 7, the lithium cobalt oxide of wherein should modifying contains 0.5 to 15 weight %'s MO_x .

12. the method of preparation of claim 11, wherein this MO_x For ZrO_2 Or B_2O_3 .

The anodal modified lithium cobalt oxide and method for making same and the lithium ion battery that are used for the lithium ion battery

The technical field

It has stratiform rock salt type (α - NaFeO₂ The type), lithium cobalt oxide (the LiCoO₂ of structure₂); Especially, relevant modified lithium cobalt oxide, when it was used as lithium ion battery anodal, this lithium ion battery had about 4.4V's the current potential that charges.

The background art

Because the excellent energy density of chargeable lithium ion battery, they extensively have been used for the for example chargeable energy of portable phone and notebook computer of portable electronic instrument at present.

Present lithium ion battery mostly uses has stratiform rock salt type (α - NaFeO₂ The type), the LiCoO₂ of structure₂ As the positive pole, for example graphite is as the negative pole for a material with carbon element, and an organic matter solution that contains Li salt is as the electrolyte. This LiCoO₂ error: 11₂ The LiCoO₂ of type structure₂ Its current potential about 3.8 to 4V that charges as anodal lithium ion battery. If this burning temperture is that about 3.5V can be dropped to the current potential that charges of the lithium ion battery that then makes the about 400 DEG Cs left and right sides. Because high burning temperture can result in LiCoO₂ The productivity descends, and the current potential that charges of the lithium ion battery that low burning temperture is unfavorable for making, consequently have then the researcher propose a hydrothermal oxidizing process (hydrothermaloxidation) under lower temperature about 160 to 300 DEG Cs prepare stratiform rock salt type LiCoO₂, the 6,399,041st B1 of United States Patent (USP) number for example. Yet the preparation of this hydrothermal oxidizing process is comparatively complicated. So, there are needs in the in the industry cycle and one kind promptly and can improve with stratiform charcoal salt type LiCoO₂ Technique as the current potential that charges of anodal lithium ion battery. This technique not only can make preparation LiCoO₂ The temperature of calcining reduce; Also can make present use LiCoO₂ Has a higher current potential that charges as anodal lithium ion battery, so the live time of extension battery.

error:11

A main objective of the invention lies in proposing a modified lithium cobalt oxide, when it is used as lithium ion battery anodal, can improve the current potential that charges of lithium ion battery, for example 4.4V.

Another purpose of the invention lies in proposing a modified LiCoO_2 The method of preparation.

A purpose again of the invention lies in proposing a lithium ion battery its current potential that charges that has the improvement, for example 4.4V.

In order to realize above-mentioned invention purpose, the modified lithium cobalt oxide of accomplishing according to the invention contains: lithium cobalt oxide particle and attach to the MO on the surface of this granule_x, wherein M is Zr, Ti, B, Al or Ga; And when M is Zr or Ti, $x=2$, and work as M and be B, when Al or Ga, $x=3/2$.

The invention proposes a lithium ion battery, contains a positive pole, and this positive pole contains the modified lithium cobalt oxide of the invention.

The invention also proposes the method of preparation of a modified lithium cobalt oxide, contains to flood lithium cobalt oxide particle in one to contain Zr, and Ti, B is in the Al or the Ga ionic aqueous solution; And calcine gainedly by impregnated lithium cobalt oxide particle.

The preferred, the lithium cobalt oxide of should modifying contains 0.5 to 15 weight %'s MO_x . If MO_x Content be lighter than 0.5 weight %, should modified lithium cobalt oxide compare and does not produce substantial modified effect in lithium cobalt oxide. If MO_x Content be greater than 15 weight % and then probably be unfavorable for the anodal performance of modified lithium cobalt oxide as the lithium ion battery.

The preferred, this MO_x For ZrO_2 Or B_2O_3 .

In the method of preparation of the invention, the preferred, this lithium cobalt oxide particle is flooded (the NO in ZrO_3)₂ The aqueous solution or the boric acid aqueous solution.

The preferred, should by dry under a rising temperature, be calcined 1 to 5 hour 400 to 800 DEG Cs more earlier by impregnated lithium cobalt oxide particle in the method of preparation of the invention, the better calcines 3 hours about 600 DEG Cs.

The description drawings

Fig. 1 is the photo of the SEM (SEM) of lithium cobalt oxide particle.

Fig. 2 scatters spectrum (EDS) for the energy of lithium cobalt oxide.

Fig. 3 is the photograph of the SEM (SEM) of the modified lithium cobalt oxide particle of the invention

The piece.

Fig. 4 scatters spectrum (EDS) for the energy of the modified lithium cobalt oxide of the invention.

Fig. 5 is the mapping of the battery volume of discharging the specific capacitance (discharge specific capacity) to the charge-discharge cycle index, wherein a) use to adhere to and have $B_2O_3LiCoO_2$ Positive pole as the lithium ion battery; B.) the use is adhered to has ZrO_2LiCoO_2 Positive pole as the lithium ion battery; C.) use a $LiCoO_2$ Commodity are as the positive pole of lithium ion battery.

Concrete embodiment

The elaboration of the concrete embodiment of preferred

The invention is with the synthetic $LiCoO_2$ of chemical modification technique $LiCoO_2-MO_x$, wherein M and X's definition is the same. $LiCoO_2$ The method of preparation to be industry institute known, a typical case's method of preparation is including mixing solid-state industrial grade lithium carbonate (Li_2CO_3) and cobaltous oxide (Co_3O_4) the granule, and calcined this mixture 5 to 25 hours 600 to 900 DEG Cs, the preferred calcine 10 hours 800 DEG Cs, form pure looks $LiCoO_2$ The host compound. $LiCoO_2$ is further flooded with the aqueous solution of water-soluble precursor (for example zirconium nitrate or boric acid) to the invention $LiCoO_2$, calcine 1 to 5 hour 400 to 800 DEG Cs again, make M metallic ion in the water-soluble precursor behind the high temperature oxidation, form attached to $LiCoO_2$ The MO on surface $LiCoO_2-MO_x$ The oxide, that is form $LiCoO_2-MO_x$ A suitable quantity of water-soluble precursor is for making $LiCoO_2-MO_x$ The MO who contains 0.5 to 15 weight % MO_x .

Embodiment 1: $LiCoO_2-ZrO_2$

To have 90% particle diameter is lighter than the $LiCoO_2$ of 17 microns grain-size distribution $LiCoO_2$ 1.9 grams of granule flood in containing 0.1 gram $ZrO(NO_3)_2 \cdot xH_2O$ In 20 milliliters aqueous solution of O (molecular weight 231.23, ALDRICH, the United States, code name 34646-2), at 110 DEG Cs of mixtures that the drying formed, calcine 3 hours with gained dry mixing thing in 600 DEG Cs again. The anodal material of lithium ion battery can be regarded as to result after calcining after grinding.

Fig. 1 is shown to be without the $LiCoO_2$ before modifying $LiCoO_2$ The SEM photo of granule, Fig. 2 is then be its EDS spectrum. Can find out $LiCoO_2$ from Fig. 1 $LiCoO_2$ The surface of granule is fairly level and smooth, and Fig. 2 is then show oxygen and Co's peak.

The $LiCoO_2$ of modified $LiCoO_2$ The SEM photo shown in Fig. 3, from wherein can finding out $LiCoO_2$ The surface adhesion of granule has the material. Fig. 4 is the $LiCoO_2$ of this modified $LiCoO_2$ EDS spectrum, wherein

Except oxygen and Co's peak, also demonstrate Zr's peak.

Embodiment 2: $\text{LiCoO}_2\text{-B}_2\text{O}_3$

Except boric acid (the H with 0.1 gram_3BO_3 , molecular weight 61.83) powder (ALDRICH, the United States, code name 23646-2) replaces ZrO (the NO of 0.1 gram_3) $_2\cdot\text{xH}_2\text{O}$ Outside the O, the step of repeated embodiment 1.

Use embodiment 1 to 2 and commodity LiCoO_2 (Nippon chemical Industrial Co., Japan, code name CELLSEED C), the preparation is anodal, regards as the negative pole with the lithium metal, reaches the 1M LiPF with EC (ethylene carbonate) and DEC (diethyl carbonate) mixed solvent. Solution is as electrolyte, equipment 2030-Type button half cell. Test under 0.2C's charge-discharge speed (current density 28mA/g) condition. When with commodity LiCoO_2 The material is as anodal battery during with the high potential charge-discharge (3 to 4.4V), though the multiplicable battery live time of lower current potential charge-discharge (3 to 4.2V) is about 20%, finds the phenomenon like Fig. 5 (c) when long loop test, that is extremely during about 70 secondary cycles, the volume of discharging the specific capacitance fails by a wide margin. Modified LiCoO with the invention $_2\text{-MO}_x$ As anodal battery, when the same test condition, the result is shown like (the a) and (b) of Fig. 5, in 100 secondary cycles test back, when M is B, can keep the initial discharge specific capacitance volume more than 90%, and M then keeps 81% initial discharge specific capacitance volume when being Zr.